Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Xu, Xinhe , Zhou, Weidong and Li, Yuliang(2007) 'Novel Selective Receptor for SO_2 Based on Molecular Recognition', Supramolecular Chemistry, 19: 7, 525 — 529, First published on: 13 September 2007 (iFirst)
To link to this Article: DOI: 10.1080/10610270601178411
URL: http://dx.doi.org/10.1080/10610270601178411

Supramolecular Chemistry, October–November 2007 Vol. 19 (7), pp. 525–529

Novel Selective Receptor for SO_2 Based on Molecular Recognition

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(Received 17 November 2006; Accepted 16 December 2006)

A novel selective receptor for SO_2 containing pyridine-2,6-dimethylamine and pyrene units was investigated. This sensor exhibits remarkably photoluminescent quenching in the presence of SO_2 and is highly inert towards HCl and O_2, which typically affect the detection of SO_2 in industrial exhausts with common methods. Additionally, this SO_2 sensor can work in solid film as well, which is more relevant to materials applications in practice.

Keywords: Fluorescent sensor; Molecular recognition; Sulfur dioxide

INTRODUCTION

Within the past decades, revolutionary advances in supramolecular chemistry have resulted in the successful complexation and sensing of ions as well as neutral organic molecules. Surprisingly, the application of principles and techniques of supramolecular chemistry and molecular recognition to the detection of gases has rarely been exploited [1–6]. And rules governing reversible gas–receptor interactions, which are responsible for binding selectivity and chemical action, are still poorly understood. Sulfur dioxide, which is mainly formed from the burning of coal and oil, contributes significantly to the formation of acid rain and other harmful products. Therefore, detecting of SO_2 is of great concern in relation to environmental pollution, occupational health, and industrial emission control, particularly with the enforcement of stringent regulation policies [7]. To our knowledge, most SO_2 sensors are either based on pH indicators or involve the chemical reaction of SO_2 and are derived from its (bi)sulfite, with various dyes [8–16]. Here we report a supramolecular approach for the potential detection of SO_2 which shows a quenched fluorescent signal in the presence of SO_2 using exact molecular recognition.

Pyridine and SO_2 can form a weak charge-transfer complex with pyridine·SO_2 in solution at room temperature, whose dissociation constant is about 1000 times larger than that of the more stable $Me_3N{\cdot}SO_2$ complex, due to the weak basicity of pyridine [17,18]. The complex of pyridine·SO_2 will gradually decompose in solution due to the volatilization of SO_2 over time or in acid conditions. Both theory and experiments have demonstrated that pyridine and SO_2 lay in the symmetry planes forming an "L" shape with a dihedral angle of 95° in the pyridine·SO_2 complex [19]. Sulfur dioxide adopts the conformation of trigonal planar geometry with the bond-length of 1.43 Å and bond-angle of 120°. The dipole moment of free SO_2 is 1.633 D, which indicates the oxygen atoms withdraw much more electronic cloud and may act as favorable hydrogen bond acceptors. These features indicate units introduced at 2,6 positions of pyridine which could coordinate with two oxygen atoms of SO_2 will enhance the stability of pyridine·SO_2 complex. From this perspective, we considered the possibility of designing a SO_2 receptor that contained two hydrogen-bond–donor groups at the 2,6 positions of the pyridine unit. In our experiments pyridine-2,6-dimethylammonium served as a receptor for SO_2, in which, hydrogen bonds between oxygen atoms from SO_2 and protons from dimethylammonium cooperate with the N–S interactions to recognize the SO_2 molecule.

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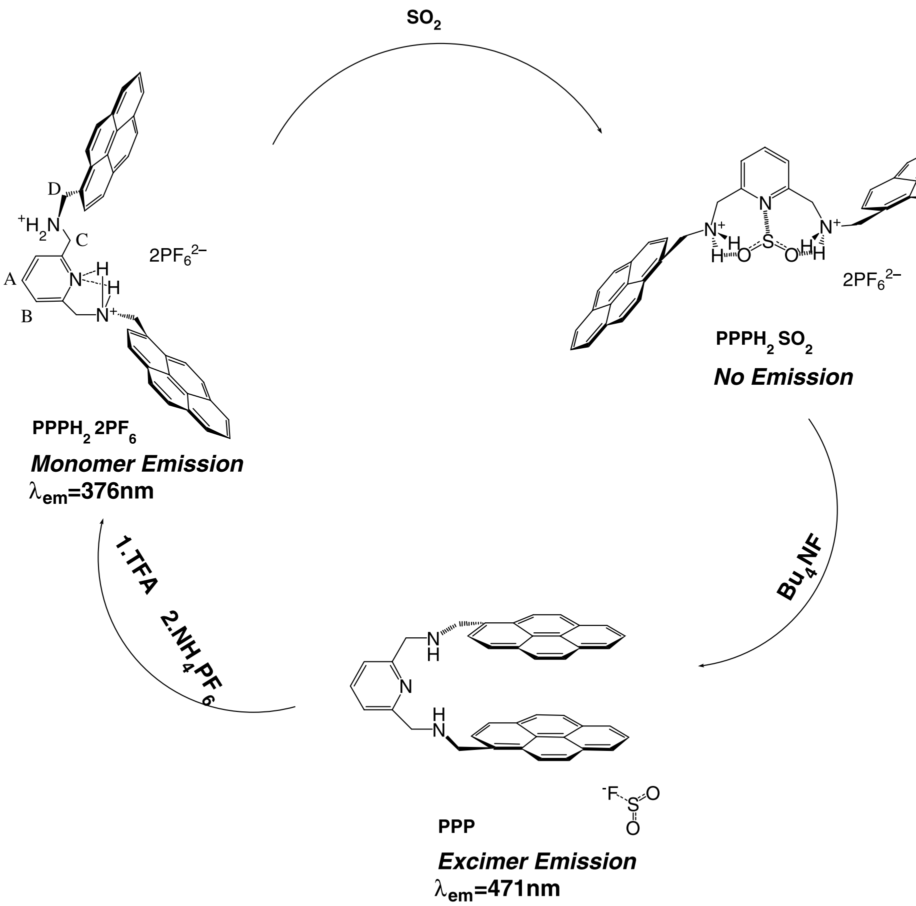
ISSN 1061-0278 print/ISSN 1029-0478 online
DOI: 10.1080/10610270601178411



SCHEME 1 An indicator-displacement assay for the detection of SO_2. **PPPH$_2$** is initially coordinated to SO_2 and then displaced by F^-.

RESULTS AND DISCUSSION

The sensor system functions as described in Scheme 1. In the absence of SO_2, 2,6-di(pyrenylmethylaminomethyl)pyridine-dihexafluorophosphate (**PPPH$_2$.PPPH$_2$·2PF$_6$**), due to strong intramolecular electrostatic repulsion between two ammonium cations, adopts a linear conformation and performs intense monomer emissions centered at 376 nm [20]. Once SO_2 is introduced the pyridine-2,6-dimethylammonium (**PPPH$_2^{2+}$**) receptor coordinates with SO_2 through N···S interactions and four-point hydrogen bonds. Furthermore, when the complex is irradiated, photo-induced charge transfer takes place between pyrenyl moieties and SO_2 which causes the fluorescent quenching of the chromophore. Upon addition of F^-, **PPPH$_2^{2+}$** receptors are displaced because of the stronger coordination ability of F^- ion with SO_2 molecule [21], And **PPPH$_2^{2+}$** was also deprotonated forming **PPP** due to the strong basicity of F^- [22,23], which leads to the formation of stable intramolecular excimer and turns on the intense emission around 470 nm.

We monitored changes in the fluorescent spectra of **PPPH$_2$·2PF$_6$** in the presence of different concentrations of SO_2 as shown in Fig. 1a. According to Fig. 1a, the plot of fluorescence intensity of **PPPH$_2$·2PF$_6$** versus the concentration of SO_2 was obtained and shown in Fig. 1b. The fluorescence intensity of monomer emission at 376 nm decreases gradually with the addition of SO_2, indicating the successful

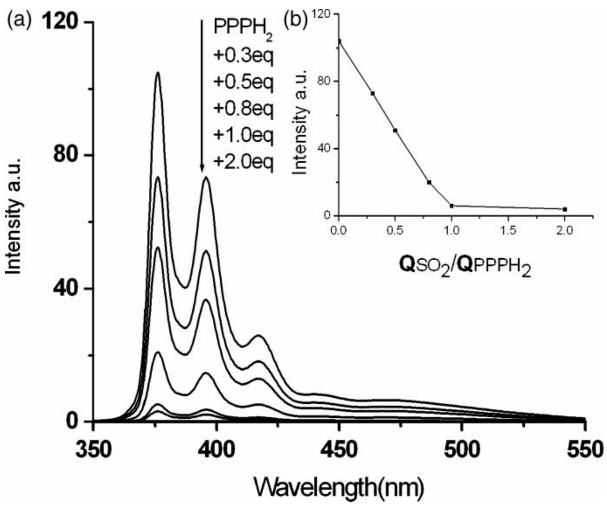


FIGURE 1 (a) Fluorescent spectra of **PPPH$_2$·2PF$_6$** (5.0 μM) upon addition of SO_2 in $CHCl_3$ at 25°C. The excitation wavelength was 344 nm. (b) The plot of fluorescence intensity of **PPPH$_2$·2PF$_6$** versus the concentration of SO_2.

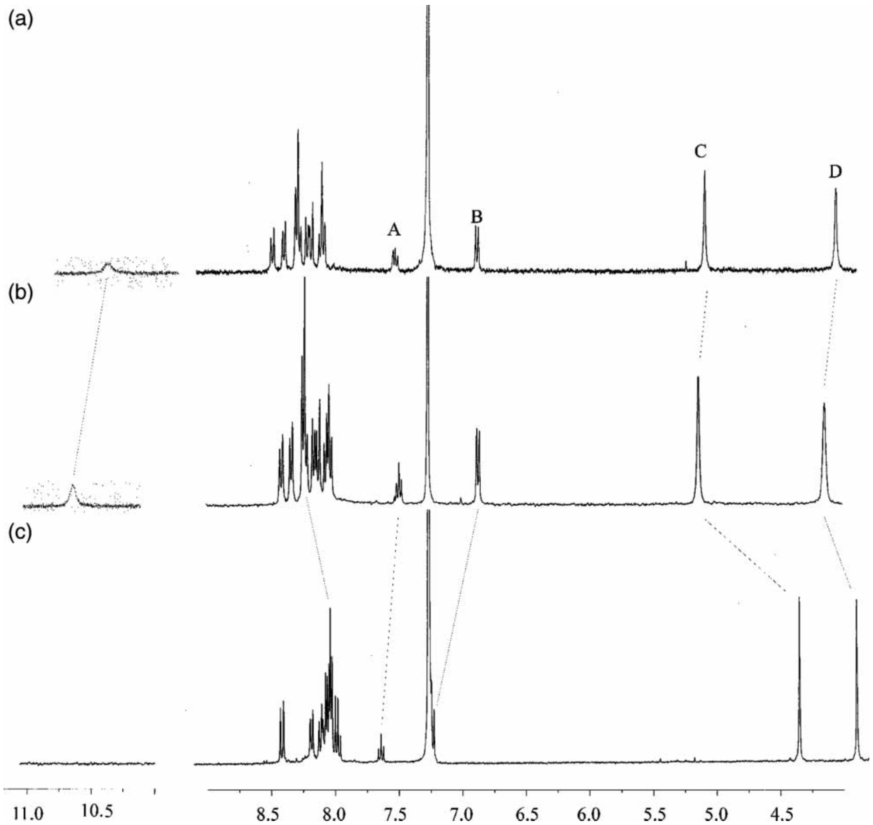


FIGURE 2 Partial ^{1}H NMR spectra (400 MHz, CDCl$_3$) of **PPPH$_2$·2PF$_6$** (a), it's complex **PPPH$_2$·SO$_2$** (b), and the mixture of Bu$_4$NF and **PPPH$_2$·SO$_2$** (c).

complexation of **PPPH$_2^{2+}$** with SO$_2$. As expected, the emission intensity of the monomer will not fall off after the addition of more than 1 equivalent of SO$_2$, which supports the 1:1 stoichiometry between **PPPH$_2^{2+}$** and SO$_2$.

The complexation process was also followed by ^{1}H NMR spectroscopy in CDCl$_3$. From Fig. 2, NMR spectra illustrated that the molecular composition remains unchanged during the complexation between **PPPH$_2$·2PF$_6$** and SO$_2$, which eliminates the possibility of a chemical reaction between them. Upon addition of SO$_2$, the ^{1}H NMR signals of the protons from diammonium notably shifted downfield by 0.3 ppm, which indicated the formation of hydrogen bonds between protons from diammonium and SO$_2$. And the signals of the pyridine protons did not experience obvious shifts, implying the effects to the pyridine protons from the charge–chansfer complex were comparable to that from the intramolecular hydrogen bonds [24–26]. The **PPPH$_2$·SO$_2$** complex can stand for many days in atmosphere at room temperature, while, the pyridine·SO$_2$ complex will decompose in 5 min under these conditions. These features demonstrated the synergistic effect from the diammonium units was important for this molecular recognition for SO$_2$, which support our design concept mentioned above.

To examine the selectivity of this sensor, we also carried out studies with other gases, such as CO$_2$, HCl, NO and O$_2$. These gases are typically mixed with SO$_2$ in industrial exhausts. Due to the existence of diammonium units and strong intramolecular hydrogen bonds, HCl does not protonate the pyridine unit in this case [27–29]. Fig. 3 shows the dependence of emission intensity of **PPPH$_2$·2PF$_6$** on the various gases. The fluorescence of **PPPH$_2$·2PF$_6$** was not influenced at all by respective addition

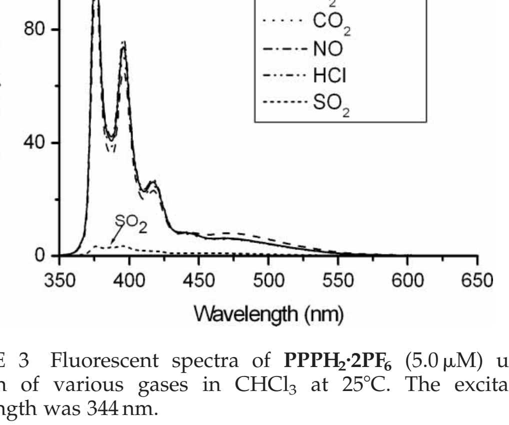


FIGURE 3 Fluorescent spectra of **PPPH$_2$·2PF$_6$** (5.0 μM) upon addition of various gases in CHCl$_3$ at 25°C. The excitation wavelength was 344 nm.

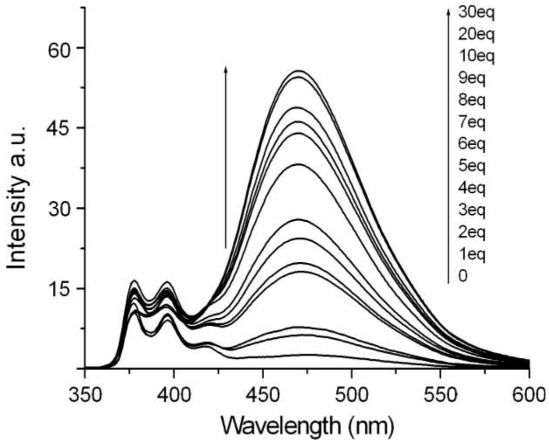


FIGURE 4 Fluorescent spectra of $\mathbf{PPPH_2{\cdot}SO_2}$ (5.0 μM) upon addition of Bu_4NF in $CHCl_3$ at 25°C. The excitation wavelength was 344 nm.

of CO_2, HCl, NO and O_2 due to the poor coordination ability of the $\mathbf{PPPH_2^{2+}}$ receptor with these gases.

To examine the recyclability of this sensor system, we added Bu_4NF to displace $\mathbf{PPPH_2^{2+}}$ by virtue of the stronger coordination ability of F^- ion with SO_2 molecule. From the ^{1}H NMR spectra, upon addition of F^-, the —NH— signal at $\delta = 10.7$ ppm disappears and the majority of signals pertinent to the $—CH_2—$ hydrogens shift distinctly upfield, with the greatest shift observed for $—C_CH$ ($\Delta\delta = 0.7$ ppm). From empirical criterion for discerning net proton transfer and true hydrogen-bond formation between an —NH— containing receptor and an anion [22,23], a net proton transfer process from $\mathbf{PPPH_2^{2+}}$ to F^- is supported. And the aromatic protons of pyrene units shift to higher magnetic fields upon the addition of excess F^-, indicating the appearance of magnetic shielding effect from the aromatic rings which supports the concept that the conformational change of two pyrene groups (see in Fig. 2). But within this system, both $\mathbf{PPPH_2^{2+}}$ and SO_2 can react with F^-, which one reacts first? In the first case, $\mathbf{PPPH_2^{2+}}$ is deprotonated with the addition of F^- initially forming **PPP** [22,23], and SO_2 will complex with the released amine, which will not affect the quenching of fluorescence in this system. With the addition of more F^-, SO_2 will complex with F^- and release the **PPP** unit exhibiting the emission of the pyrene excimer [20]. That is, the fluorescence will alternate from faintness to excimer emission directly. While, in the latter case, $\mathbf{PPPH_2^{2+}}$ unit will be replaced by F^- initially, this will turn on the emission of $\mathbf{PPPH_2^{2+}}$ at first. Then the additional F^- will act as a base to deprotonate the $\mathbf{PPPH_2^{2+}}$ unit forming **PPP** [22,23], inducing the increase of excimer emission at the expense of monomer emission. That is, the fluorescence will fluctuate from zero to monomer emission and then excimer emission in this case. As shown in Fig. 4, the fluorescence spectrum alternated from zero to excimer emission directly with the addition of Bu_4NF, which supports the former case mentioned above.

To see if the same principle could work in environments that are more relevant to application, we prepared thin transparent films of $\mathbf{PPPH_2{\cdot}2PF_6}$ on quartz slides by evaporation of solutions of $\mathbf{PPPH_2{\cdot}2PF_6}$ in dichloromethane. A broad peak at 480 nm was detected when the $\mathbf{PPPH_2{\cdot}2PF_6}$ film was illuminated with UV light (353 nm), due to the intermolecular aggregation and the formation of excimer. Exposure of the $\mathbf{PPPH_2{\cdot}2PF_6}$ coated slides to SO_2 vapor resulted in a nearly complete quenching of fluorescence on the film (Fig. 5a), which indicated that $\mathbf{PPPH_2{\cdot}SO_2}$ complex also lost its fluorescence in the solid state. As expected, when the $\mathbf{PPPH_2{\cdot}2PF_6}$ coated slides were exposed to other gases, the emission of the film was hardly affected, only slight quenching in fluorescence was detected upon exposure to NO and HCl. These results indicate that $\mathbf{PPPH_2{\cdot}2PF_6}$ coated slides also possess specific recognition ability for SO_2.

To verify the SO_2 selectivity of $\mathbf{PPPH_2{\cdot}2PF_6}$ in film, we also conducted a competitive experiment. $\mathbf{PPPH_2{\cdot}2PF_6}$ coated slides were exposed to four kinds of other gases followed by exposure to SO_2 gas. As expected, all four slides performed intense fluorescence in four gases and then became gloomy with the steaming of SO_2. These results shown in Fig. 5b clearly demonstrate a high SO_2 selectivity of $\mathbf{PPPH_2{\cdot}2PF_6}$ film.

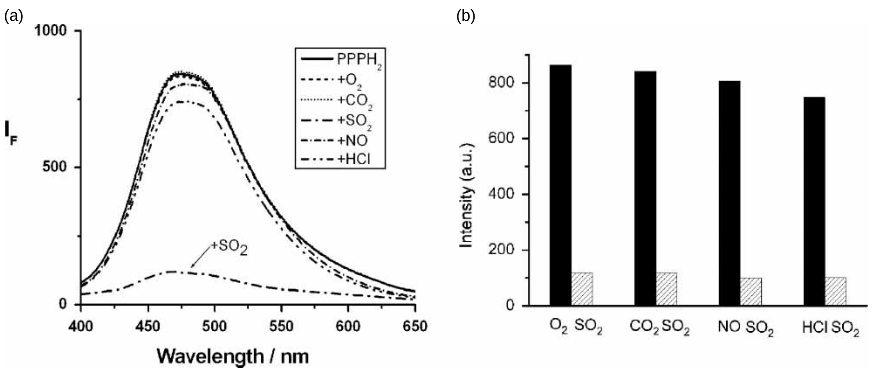


FIGURE 5 The fluorescence spectra of the quartz slides coated with $\mathbf{PPPH_2{\cdot}2PF_6}$ film upon exposed to different vapors (a), and followed by exposure to SO_2, respectively (b).

In conclusion, we present a new receptor for SO_2 based on the molecular recognition, which exhibits marked photoluminescent quenching in the presence of SO_2. This sensor is highly inert towards HCl and O_2, which typically affect the detection of SO_2 in industrial exhausts with common methods. It is worth pointing out that our SO_2 sensor can work as a solid film as well, which is more relevant to application in practice.

MATERIALS AND METHODS

The chemical reagents were purchased from Acros or Aldrich Corporation and utilized as received unless indicated otherwise. All solvents were purified using standard procedures. UV-vis spectra were taken on a Hitachi U-3010 spectrometer and fluorescence spectra were measured on a Hitachi F-4500 spectrofluorometer. ^1H NMR spectra were obtained on a Bruker Avance DPS-400 spectrometer.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (20531060, 10474101, 50372070, 20418001, 20473102) and the Major State Basic Research development Program (2006CB806200, 2005CB623602).

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